

Enhancement of 3-Way CNG Catalyst Performance at High Temperature Due to the Presence of Water in the Feed: On the Role of Steam Reforming of Methane and on the Influence of Ageing

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Abstract The reaction mechanism of typical 3-way catalysts (TWC) has been already deeply studied. However, fewer efforts have been made to understand TWC compressed natural gas applications. Thus, the role of water in reducing atmospheres is still not well understood. In the present paper we show the positive impact of water on pollutants abatement at high temperature on commercial converters.

Keywords Three way catalysis · Natural gas · Palladium · Methane steam reforming

1 Introduction

Rigorously regulated automotive exhaust gas emissions according to standards as Euro 4 (in effect since January 1, 2005) or Euro 5 (September 1, 2009), demands the employment of efficient strategies for emission reduction. Natural Gas (NG), primarily composed by methane, is regarded as one of the most promising alternative fuels: natural gas engines produce lower particulate matters (PM)

than diesel and for NG combustion lower combustion temperatures are required which leads to a decrease of NO_x emissions [1]. However, methane is the major hydrocarbon exhaust component and the most difficult to catalytically oxidize. Three-way catalysts, which are known as effective for simultaneous NO_x , CO and HC removal by their interaction with noble metals as Rhodium, Platinum and Palladium. Moreover, palladium has gained especial attention particularly for compressed natural gas (CNG) vehicles applications due to its high performance for methane abatement in lean or stoichiometric conditions [2–4]. In the last years, authors focalized essentially on the understanding of mechanism and kinetic of the reactions $\text{CO} + \text{O}_2$, $\text{CO} + \text{NO}$ and $\text{HC} + \text{NO}$ separately. However, the exhaust gases are not only composed by the three major pollutants and has been observed that for a gasoline 3-way catalyst, water presence in the exhaust gas (up to 10%) play a very important role as oxidant of unburned hydrocarbons [5]. The aim of this work is to understand the role of water on the methane treatment at high temperatures during the exhaust gas treatment using a commercial 3-way Compressed Natural Gas (CNG) catalyst. Moreover, Recently, Winkler et al. [6] showed that on bifuel commercial converters that after 35,000 km mileage some differences are observed. Indeed, a loss of activity is observed after that mileage. On used converter a Pd layer has formed on a PdO core whereas the new TWC contained pure palladium oxide. Moreover, contaminants like P, Ca and Mg, originating from the lubricating oil, were found on both vehicle aged catalysts. Si, not contained in the lubricating oil, was only detected on the pre-catalyst. Finally, the vehicle aged pre-catalyst lost 95% of its original surface area, whereas the underfloor catalyst only lost about 50%. Thus, we also try in this work to understand the loss of activity of commercial catalysts.

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2 Experimental

2.1 Catalysts Samples

The commercial catalytic converters (A and B) extracted from a compact and a station wagon CNG vehicle are first cut to obtain 2 different monoliths with 1 in. of diameter and 1.9 in. of length. Before each run phase, these monoliths were calcined ex-situ under air ($200 \text{ cm}^3 \text{ min}^{-1}$) at 500°C . The catalyst was then placed in the metallic reactor and flushed in synthetic air ($80\% \text{N}_2/20\% \text{O}_2$) prior each test. One used A converter, denoted A', was also studied with 20,000 km mileage.

2.2 Characterization and Catalytic Activity Analysis

These commercial converters are analyzed by different techniques such as elementary analysis, Transmission Electronic Microscopy, Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy. More details are reported elsewhere [3].

All the activity runs were carried out using a synthetic gas mixture device. For all the tests, honeycomb catalysts are used, the gas hourly space velocity is equal to $40,000 \text{ h}^{-1}$. During the light-off, the temperature ramp is equal to $10^\circ\text{C min}^{-1}$. The gas mixture was realized using a bench of mass flow controllers. The reaction mixture which is representative of exhaust gases composition, is

composed by: 0.25% NO , 0.17% CH_4 , 0.48% of O_2 , 9.25% CO_2 , 0.47% CO , 0.34% H_2 and 18% H_2O , with a richness of 1,005 passed through a pre-heater in which the temperature was controlled.

The heated gases were sent through the reactor. The reactor outflow was analyzed using the combination of different detectors and all the collected data were treated with virtual bench National Instruments Software. In order to evidence the role of water, other runs were performed in the presence of 0.17% CH_4 and 18% H_2O with a GHSV fixed at $40,000 \text{ h}^{-1}$.

3 Results and Discussion

3.1 On the Effect of Ageing on Commercial NGC Converters

By Elementary Analysis, noble metals such as palladium (2.55 wt%), rhodium (0.18 wt%), but also cerium (2.15 wt%), zirconium, lanthanum, barium are detected for catalyst A [4] (Table 1). The BET surface of this catalyst was equal to $110 \text{ m}^2 \text{ g}^{-1}$.

After only 20,000 km of mileage, a loss of noble metals is observed. In fact, only 1.76 wt% of palladium and 0.14 wt% of rhodium were found, a loss of surface area was also observed ($77 \text{ m}^2 \text{ g}^{-1}$). For a sake of comparison, on the catalyst B, no platinum was detected whereas the loadings of palladium and rhodium were 0.7 and 0.08 wt%, respectively. The BET surface of catalyst B is $104 \text{ m}^2 \text{ g}^{-1}$.

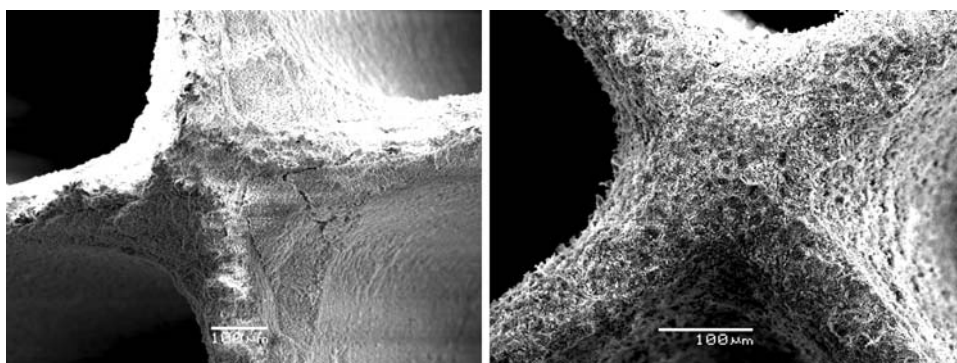
The loss of metal content between fresh and used catalysts (A) could be explained by different phenomena. We could point out a washcoat adhesion failure as presented in Fig. 1. Thus, one can see large differences in the washcoat morphology in Fig. 1. In the Right, on the aged catalyst, a loss of washcoat and failures are observed.

This phenomenon is responsible for the loss of 30% of noble metals according to Elementary Analysis. The loss of activity can be correlated with the decrease of catalyst activity as function of mileage as presented in Fig. 2.

Table 1 Metal contain on the fresh and used catalyst (wt%)

ICP analysis	Fresh catalyst	20,000 km used catalyst
Pd	2.55	1.76
Rh	0.18	0.14
Pt	0.07	0.06
Ce	2.14	1.94
Al	23.98	21.44

Fig. 1 SEM analysis of fresh (on the left) and used (on the right) honeycomb catalyst A



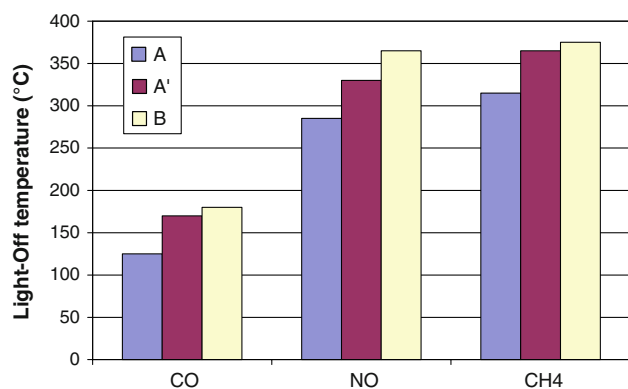


Fig. 2 Comparison of light-off temperature for different honeycomb converters (A), (A') after 20 000 km mileage, comparison with a low PMG loading catalyst (B)

Another point can explain the decrease of catalytic activity: the sintering of palladium particles. Thus, by TEM, the sintering of palladium particles is observed. The average particles size of PdO increases from 2 nm for fresh catalyst to 40 nm after 20,000 km of mileage (Fig. 3). By HRTEM, only PdO phases were found (Figure not shown).

By XPS, the same phenomena were observed: a decrease of noble metals is observed at the surface. No more rhodium is detected after 20,000 km mileage. These results are in agreement with those obtained by ICP and TEM.

The oxidation state of palladium is always found as +II. No Pd in zero oxidation state is observed even after 20,000 km. These results confirm that the main phase at the surface is PdO, even we can not exclude the presence of Pd_xO_y phases.

As already reported in other CNG experimental conditions, the catalytic runs (Fig. 2) revealed that the light-off temperatures (T_{50}) of CO, NO and methane are shifted to higher temperatures (up to 65 °C), for a catalyst with a mileage of 20,000 km [7].

However, the catalytic activity of used catalyst is still higher than those obtained for low loading PMG catalyst B. One can propose that the catalytic activity is related to noble metal loading; however we will show that the overall

activity is related to the Steam reforming of methane occurring on these catalysts during the global process.

3.2 On the Effect of Water on Commercial NGC Converter

After performing a temperature programmed reaction run with the complete reaction mixture it was possible to observe that with catalyst A, being the most active leading to lower light off temperatures, methane conversion to CO₂ is total (Figure not shown). In what concerns catalyst B and comparing the noble metals contents of both catalysts, this catalyst also leads to very interesting results for NO_x and CO elimination ($T_{loA} = T_{loB} + 30$ °C). However, after total conversion of NO in N₂, the CH₄ conversion stops and at 500 °C reaches a maximum of conversion of 60%.

Thus, a second experiment was performed in order to study the reaction between methane and water over these two catalysts. And, a comparison was made with the used catalyst A' (Fig. 4). According to Fig. 4, with catalyst A, methane starts interacting with water from 250 °C. At 500 °C all the amount of HC supplied is reacting with water. The reaction occurring is mainly the steam reforming of methane: $CH_4 + H_2O = CO + 3H_2$.

However, never CO is observed, thus, water gas shift reaction also occurs in this temperature range.

The Catalyst B, however, is not so active for the reaction of steam reforming of methane, with a maximum conversion of 50% reached at 310 °C.

Concerning the hydrogen production, followed by mass spectrometry ($m/z = 2$), one can see that the hydrogen production is increasing with the temperature for the catalyst A even with 20,000 km mileage. However, once again, on the converter B, the hydrogen production reached a maximum then stabilized up to the high temperatures. We recently proposed that in CNG conditions, the hydrogen is the main reducing agent of NO at low and medium temperature and the methane is the one at high temperature [3]. One can now suppose that from methane steam reforming

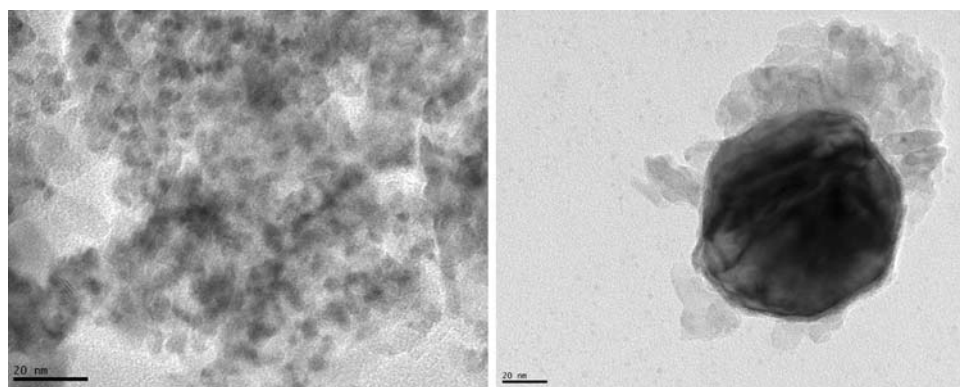


Fig. 3 TEM analysis of fresh and used honeycomb catalyst A

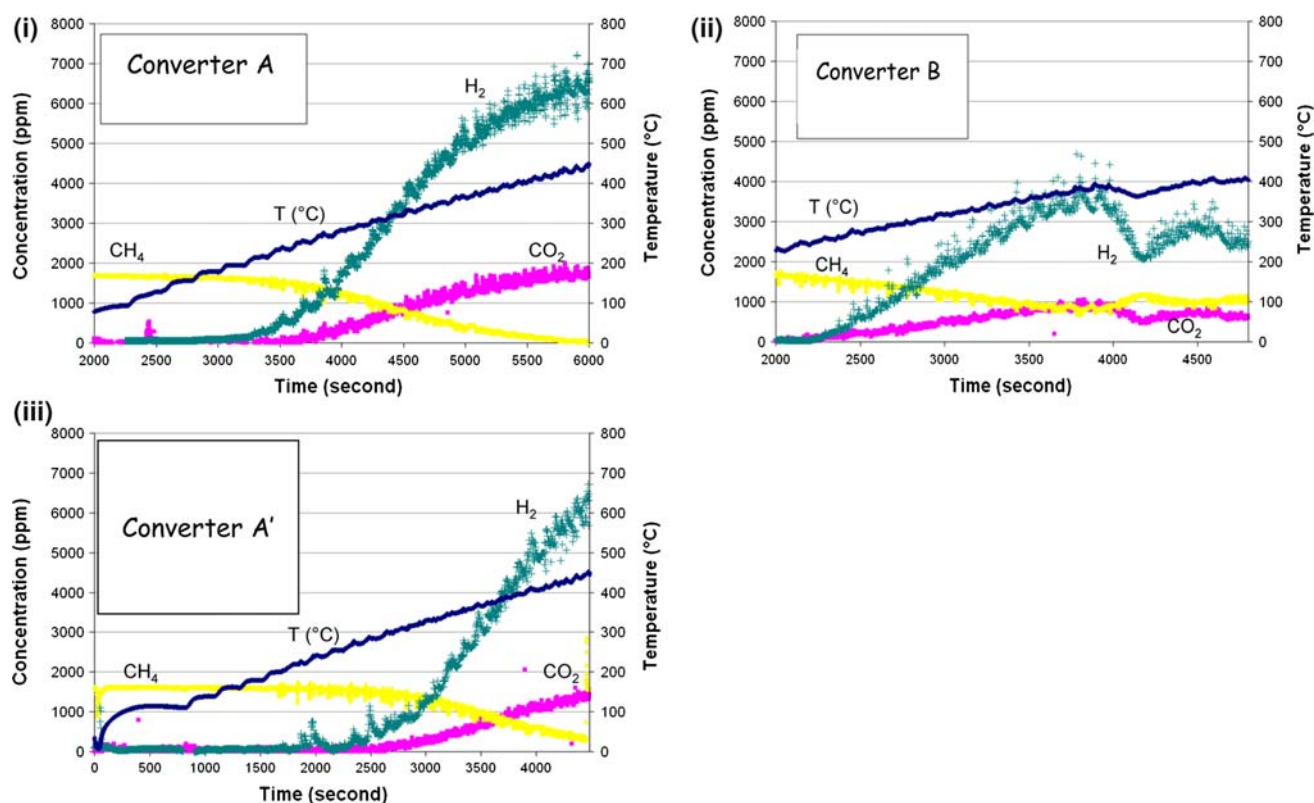


Fig. 4 CO_2 , H_2 and CH_4 profile during temperature programmed reaction in the presence of 0.17% of methane and 18% of H_2O with catalyst A (a) and B (b), comparison with used converter A' (c) in monolithic form

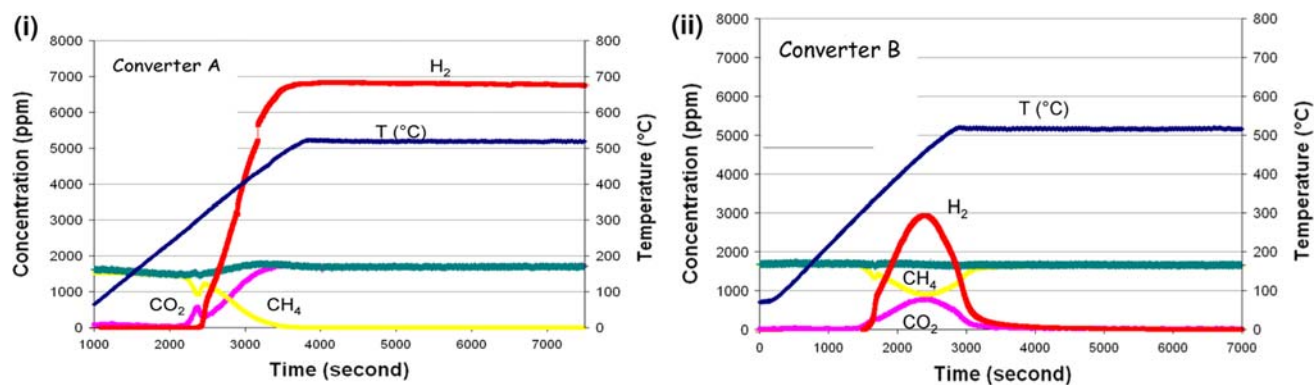


Fig. 5 CO_2 , H_2 and CH_4 profile during temperature programmed reaction in the presence of 0.17% of methane and 18% of H_2O with catalyst A (a) and B (b), comparison with used converter A' (c) in powder form

hydrogen is produced in-situ and this hydrogen becomes then a new reducing agent of NO at high temperature. Thus, the steam reforming of methane is one key reaction on the Three-way catalytic process in CNG conditions. In order to confirm these results, we performed the same reaction on the active phase from the commercial catalysts (Fig. 5). A Light-off study was followed by a steady-state study in isothermal conditions at 500 $^{\circ}\text{C}$.

One can see, from Fig. 5 that the steam reforming of methane only occurred on the active phase of converter A in steady state conditions. On converter B, the reaction

occurred during the Light-off reaction but then stopped. A more detailed study is in course to explain this non reaction on converter B.

4 Conclusions

This study deals with the evolution of commercial TWC CNG catalyst in a synthetic gas mixture. The loose of activity is not only due to sintering of PMG particles, mainly PdO, but also to a loose of noble metals and a degradation of

washcoat. Actually a study is in course in order to simulate at laboratory scale the mileage of 20,000 km.

The presence of water in the exhaust CNG vehicles seems to have a major importance for the abatement of methane in rich conditions at high temperatures. The low methane conversion obtained with catalyst B leads us to conclude that the presence of Pd in PdO_x form is necessary not only for the reaction between NO and methane but also for the steam reforming reaction that is essential for the total consumption of methane in rich atmospheres.

From this study, we also showed that steam reforming of methane is essential on global TWC process dedicated to CNG applications, since hydrogen is the main reducing agent in these conditions. Thus, this reaction could be a good probe reaction in order to find a better CNG commercial catalyst.

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